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(54) Liquid polymer and liquid copolymers of Butadiene and the preparation thereof.

(57) Liquid polymers and liquid copolymers of butadiene useful as surface coatings and constituents of surface coating compositions, are prepared by subjecting butadiene or a mixture of monomers comprising a major proportion of butadiene to an anionic telomerisation step in the presence of at least one hydrocarbyl lithium compound, at least one chain transfer-promoting catalyst and at least one chain transfer agent to form a mixture of active macromolecular carbanions and linear or substantially linear and ionically inert macromolecules. At least a proportion of the macromolecular carbanions is then reacted to form a multi-arm star polymer or copolymer in the presence of the inert macromolecules, the star polymer or copolymer comprising at least 5% of the total weight of the resulting polymer or copolymer. The linking compound may be one having three or more reactive sites capable of linking with a polymeric carbanions or may be one which has at least two functional groups per molecule and which is capable of polymerisation to form a nucleus to which the polymeric carbanions are attached.



## SPECIFICATION

**Liquid polymers and liquid copolymers of butadiene and the preparation thereof.**

5 This invention relates to the preparation of liquid polymers and liquid copolymers of butadiene which are useful for surface coatings and as constituents of surface coating compositions.

10 According to one aspect of the present invention there is provided a process for the preparation of a liquid polymer of butadiene or a liquid copolymer of butadiene, wherein butadiene or a mixture of two or more monomers comprising a major proportion of butadiene is subjected to an anionic telomerisation step in the presence of at least one hydrocarbyl lithium compound, at least one chain transfer-promoting catalyst and at least one chain transfer agent, thereby to form a mixture of active macromolecular carbanions and linear or substantially linear and ionically inert macromolecules, and wherein, in a further step, at least a proportion of the macromolecular carbanions is reacted with a linking compound to form a multi-arm star polymer or copolymer in the presence of the linear or substantially linear inert macromolecules, said star polymer or copolymer comprising at least 5% of the total weight of the resulting polymer or copolymer.

25 According to another aspect of the present invention there is provided a liquid polymer of butadiene or a liquid copolymer of butadiene prepared by the process just defined.

30 The term "liquid polymer of butadiene" is used herein to mean a polymer produced by the process of the invention employing butadiene as the sole anionically polymerisable monomer during the telomerisation step, and the term "liquid copolymer of butadiene" is used herein to mean a copolymer produced by the process of the invention employing during the telomerisation step two or more anionically copolymerisable monomers of which one is butadiene and the other or others is or are other monomers, examples of which include isoprene and other conjugated dienes, styrene and other mono-  
45 vinyl aromatic compounds and alpha-methylstyrene. The viscosity of the aforesaid liquid polymer or copolymer desirably does not exceed 2500 poise at 30°C. and the proportion of butadiene in 100 parts by weight of monomers is not less than  
50 50 parts by weight.

The anionic telomerisation step which is employed in the present process is conventional. In order to explain the nature of the present invention, the chemistry of the reactions involved will be described in essence, although in detail it is considerably more complex than appears from the explanation which is not to be taken in such a way as to limit the scope of the invention.

Anionic telomerisation comprises the four following reactions:

1. *Initiation*, involving molecules of monomer and molecules of at least one hydrocarbyl lithium compound which is introduced or which has been formed at the beginning of the telomerisation step,  
65 and which may be either a low or a high molecular

weight hydrocarbyl lithium compound including both mono- and polythio hydrocarbons, this reaction resulting in the formation of carbanions.

2. *Propagation*, involving repeated addition to carbanions of molecules or butadiene together with molecules of any other copolymerisable monomers which may be present.

3. *Chain transfer*, involving carbanions formed as a result of propagation and molecules of one or more chain transfer agents, whereby the carbanions abstract protons from molecules of chain transfer agent such that ionically inert macromolecules are formed together with carbanions comprising residues of the molecules of chain transfer agent.

4. *Re-initiation*, involving the carbanions formed as a result of chain transfer.

As indicated above, the initiating hydrocarbyl lithium compound may be a low molecular weight substance such as *n*-butyl or sec-butyl lithium, or may be a polymeric lithiohydrocarbon such as polybutadienyl or polystyryl lithium and may be a mono or poly-lithiohydrocarbon. In any case, the reaction conditions can be so arranged that, if desired, all or some of said hydrocarbyl lithium compounds can be made to react first with the chain transfer agent rather than with the monomer, e.g. before monomer is added and before commencing the telomerisation stage. That is to say, from the start of the telomerisation step the initiating hydrocarbyl lithium compound can be made effectively an anion comprising a residue of a molecule of the chain transfer agent; for example, benzyl lithium when the chain transfer agent is toluene. Alternatively, the initiating compound or compounds may be allowed to react directly with monomer.

The chain transfer reaction may be repeated again and again many times for each molecule of hydrocarbyl lithium group originally present at the commencement of the telomerisation stage. Anions derived from molecules of the chain transfer agent are thus generated repeatedly and rapidly re-initiate the reaction, while macromolecules of inert telomer are formed simultaneously with these anions as a result of intermittent chain transfer. Thus, as increasing amounts of inert telomer are formed, the nature of the chemical composition of the original hydrocarbyl lithium initiator becomes less and less significant with respect to the composition of all the telomer formed. An increasing majority of the terminal groups in the polymer have their origin in residues of molecules of the chain transfer agent.

Considerable economy becomes possible in the amount of hydrocarbyl lithium initiator required per unit weight of polymer compared with reactions whereby each hydrocarbyl lithium group gives rise to only one macromolecule. This advantage is of great importance for the preparation of liquid polymers and copolymers of butadiene; such macromolecules are usually linear or nearly linear, that is to say, they contain no branches or very few branches per macromolecule.

Thus at any given moment during the telomerisation stage, the polymeric products comprise the inert macromolecules of telomer together with polymeric carbanions which are either undergoing sequential



addition of monomer units to the active ionic end of the macromolecule or intermittently are reacting with molecules of the chain transfer agent. Since there is no spontaneous termination reaction, the number of active carbanions does not change during the telomerisation step, provided that oxygen, carbon dioxide, moisture and other substances which decompose carbon-lithium bonds are excluded, and, at any given time, the reaction product comprises the inert macromolecules of polymer or copolymer in increasing concentration and a constant number of polymeric carbanions in reducing concentration.

In order to promote the chain transfer reaction at the expense of the propagation reaction, in order to secure acceptably low molecular weights, the present in adequate concentration is essential of a chain transfer-promoting catalyst. Suitable chain transfer-promoting catalysts can be classified in one or two main groups:

- (a) organic compounds of sodium, potassium, rubidium and caesium. The alkoxides of sodium and potassium are especially convenient and effective;
- (b) organic Lewis bases, such as ethers and amines, especially chelating bifunctional diamines such as tetramethylethylenediamine, but including by way of exemplification tetrahydrofuran; dimethoxydiethyleneglycol and diethylaminoethoxyethane.

One or more chain transfer-promoting catalysts may be present at the same time.

The velocity constant for the propagation reaction is much greater than that for the chain-transfer reaction, i.e., the rate of addition of units of monomer to the polymeric carbanion is much greater than the rate of reaction of chain-transfer agent with the macromolecular carbanions. In order to ensure that the former rate is subdued relative to the latter, i.e., in order to secure acceptably low molecular weights, the proportion of chain transfer-promoting catalyst or catalysts is regulated, the reaction conditions adjusted, and the concentrations of reactants controlled in such a way as to obtain the desired average molecular weight. Since molecules of monomer and of chain transfer agent are in effect competing for reaction with the polymeric carbanions, and reaction with the former is kinetically more favoured, conditions are maintained such that the concentration of chain transfer agent is always high and that of the monomer or monomers low at any given moment. These conditions are achieved by adding monomer or monomers gradually, at substantially the same rate at which they are consumed by the propagation reaction.

Chain transfer increases in rate more rapidly with increasing temperature than does the propagation rate, hence an increasing temperature yields lower molecular weights if all other parameters are unchanged.

Practical examples of the results of varying these reaction conditions, and detailed exemplification of the organolithium initiators, of the chain transfer-promoting catalysts and of possible chain transfer agents are described in British Patent Specification Nos. 1,288,057, 1,342,101 and 1,383,247.

The further step of the present process comprises

a reaction whereby at least some of the active macromolecular carbanions present in the reaction zone are linked into star polymers or copolymers consisting structurally of a nucleus or linking residue to which are attached a minimum of three macromolecular arms. It is not required that all the active polymeric carbanions present at the end of the telomerisation step shall be thus linked in order to prepare the present liquid polymeric compositions but the nature of the linking compound and the proportions thereof relative to the number of polymeric carbanions present at the time of addition of the linking compound, together with the conditions for the linking reaction, should be so selected that from 5 to 50% of the total weight of polymer or copolymer and preferably from 10 to 25% of the total weight of polymer or copolymer present after the linking step, should comprise a star polymer and copolymer as defined above.

If the proportion of polymer or copolymer linked into star-shaped macromolecules is less than about 5% of the total weight of polymer or copolymer formed at the end of the present process then the product will not show advantageous properties compared with the liquid telomer formed by the telomerisation step alone. On the other hand should the proportion of star polymer or copolymer amount to more than about 50% by weight of the total amount of polymer or copolymer formed after the linking step, then the raw material costs of the product of the process is likely to be uneconomic since each equivalent of the expensive hydrocarbyl lithium initiator will have participated in relatively few chain transfer reactions during the telomerisation step of the process.

Any compound may be used which is capable of linking the macromolecular carbanions into star-shaped macromolecules, giving a yield of the latter type of polymer or copolymer in the reaction product sufficient to comply with the quantitative composition specified above. A large number of such compounds has been described and vary widely in their efficiency for reaction with polymeric carbanions to form star polymers or copolymers, assessing linking efficiency by such parameters as the proportion of macromolecular carbanions which become linked into star polymers or copolymers for a given molar proportion of linking compound relative to the number of arms in the star macromolecules. Examples of such linking compounds are given in the following list which is not intended to be exhaustive. In the following list, compounds in groups 1 to 6 each contain at least three reactive sites and can react with the ions present in such a way as to destroy them partially or completely with the elimination of such compounds as lithium halides, lithium alkoxides, etc., at least three polymeric carbanions becoming linked simultaneously to each residue of linking compound. Linking compounds in groups 7 to 10 react by anionic polymerisation to form a nucleus to which the polymeric carbanions become simultaneously linked.

1. Tetrachlorosilane.
2. Tetrachloro tin.
3. Phosphorus trichloride.

4. Polyhalo organosilanes, such as methyl trichlorosilane, 1,2-bis(methyldichlorodisilyl)-ethane, 1,2-bis(trichlorodisilyl)-ethane, 1,2-bis(trichlorosilyl)ethane, tetra(methyl-dichlorosilylethyl)silane and
  - 5 tetra(trichlorosilylethyl)silane.
  5. Polyhalohydrocarbons, such as 1,2,4-tri(chloromethyl)benzene, 1,2,4,5-tetra(chloromethyl)benzene and hexa-[p-(chloromethyl)phenyl]-benzene.
  - 10 6. Polyesters, such as dimethylphthalate and glycerol tristearate.
  7. Polyisocyanates, such as 1,6-hexamethylene di-isocyanate and diphenylmethane di-isocyanate.
  8. Polyepoxides, such as epoxidised linseed oil.
  - 15 9. Any isomer of vinyl pyridine.
  10. Any isomer of divinylbenzene.
- In carrying out the present process, it is a requirement that the polymeric product after the linking step which includes unlinked telomer should be
- 20 liquid, that is to say, should have a viscosity not exceeding about 2500 poise at 30°C. Since the linking step must tend to cause an increase in viscosity due to the increase in the average molecular weight of the macromolecules, the viscosity of the telomer
  - 25 formed by the telomerisation stage should not be excessive. The possibility is not excluded of the star polymer or copolymer being solid or by itself having a viscosity exceeding 2500 poise at 30°C. so long as it remains completely miscible with the remainder of
  - 30 the product of the process.
- The number of polymeric carbanions present just before the linking step may be taken equal to the number of hydrocarbyl lithium bonds in the initiating compound or compounds originally present. The
- 35 quantity of linking compound required to be added can then readily be calculated from the known efficiency of linking as disclosed in the prior art. For example, one molecule of silicon tetrachloride is capable of linking four polybutadienyl carbanions
  - 40 into a four-armed star polymer, and for steric reasons three polyisoprenyl carbanions into a three-armed star. The possibility is not excluded of altering for any reason the composition of the polymer or copolymer formed during the telomerisation step. In
  - 45 particular, it may be desirable for such reasons as enhanced linking efficiency, or reduced reaction product viscosity, to alter the composition of the monomer or monomers added in such a way that the macromolecular carbanions which are to be
  - 50 linked into star macromolecules have a different constitution from that of the inert polymer or copolymer. Alternatively, only the last segments of the macromolecular carbanions may be made different in constitution in the interests of more efficient
  - 55 linking.
- A preferred linking substance is divinylbenzene in a commercially-available mixture of isomers, preferably in a proportion of at least 3 molecules of divinylbenzene per active carbanion, since such
- 60 proportions give rise to a very high proportion of macromolecules linked into star structures having an average of at least 4 arms. Increasing proportions of divinylbenzene tend to give rise to increasing average numbers of arms.
  - 65 It is surprising that star-structured macromole-

cules are formed in high yield in the presence of both chain transfer agents and chain transfer-promoting catalysts. It may be necessary to adjust the reaction conditions in order to ensure that the macromolecular carbanions do not react with the chain transfer agent after all the monomer has been consumed and before the linking compound or compounds are added, for example, by lowering the temperature immediately after all the monomer has been added, but it is a surprising finding that such precautions are often not necessary in order to secure an adequate proportion of star-structured macromolecules.

The maximum proportion of polymer in the form of star-structured macromolecules may be determined by withdrawing a sample of the liquid polymer formed at the end of the telomerisation step and determining its molecular weight by any convenient method, such as vapour phase osmometry or gel permeation chromatography. Assuming that the number of carbanions present is the same as the number at the beginning of the telomerisation step, and assuming that all the carbanions are in the form of polymeric ions, having a molecular weight as determined, and that all these carbanions are linked into star-structured macromolecules by the linking compound, the necessary calculation can readily be made.

The polymers and copolymers obtained by the process of the invention may also be investigated by gel permeation chromatography in order to determine the proportion of star-structured macromolecules and their approximate molecular weights. The invention will now be illustrated by the following Examples.

#### Example 1

Dry, distilled toluene (1500 g) was charged to a jacketed stainless steel 5 litre reactor equipped with a nitrogen inlet, a butadiene inlet, a stirrer, a dry ice/methanol condenser and a temperature probe. The temperature was raised to 70°C with stirring while the reactor was continuously purged with nitrogen. *n*-Butyl lithium (0.066 moles), as a 15 wt % solution in hexane, and potassium *t*-butoxide (0.0066 moles) as a chain transfer-promoting catalyst were charged to the reactor and the addition of butadiene was commenced at a rate of 3.5 litre/min. while the temperature was allowed to rise to 78°C.

After 215 minutes the butadiene flow rate was reduced to 1.5 litre/min. and the polymerisation mixture was cooled to 50°C. The butadiene addition was ceased and, after allowing the mixture to react out for 5 minutes, divinylbenzene (0.264 moles) was added over a period of 1 to 2 minutes as a dry 27.5 wt.% solution in an ethylvinylbenzene/toluene mixture. After stirring for a further 15 minutes the polymerisation mixture was deactivated by the addition of a proton donor.

Removal of catalyst residues and toluene yielded 1708 g. of a liquid polymer having a Brookfield viscosity of 365 poise at 25°C. a vinyl 1,2 content I.R. analysis of 24%, and a high molecular weight fraction content by gel permeation chromatography

analysis of 14.9 wt. %.

By comparison, a telomer product prepared under identical conditions but without the addition of divinyl-benzene had a viscosity of 100 poise and no evidence of any high molecular weight fraction.

#### Example 2

The polymerisation was carried out as described in Example 1 but with the following variations in the divinylbenzene linking step.

After 215 minutes, the butadiene flow rate was ceased completely and the butadiene allowed to react out for 5 minutes whilst maintaining the temperature at 78°C., Divinylbenzene (0.264 moles) was added over 10 minutes as a dry, 55 wt. % solution in ethylvinylbenzene and the polymerisation mixture cooled to 45°C., After stirring for 60 minutes the polymerisation mixture was deactivated by the addition of a proton donor.

Removal of catalyst residues and toluene yielded 1808 g. of liquid polymer having Brookfield viscosity of 340 poise at 25°C. a vinyl 1,2 content 23%, and a high molecular weight fraction content by gel permeation chromatography analysis of 16.2 wt. %.

#### CLAIMS:

1. A process for the preparation of a liquid polymer of butadiene or a liquid copolymer of butadiene, wherein butadiene or a mixture of two or more monomers comprising a major proportion of butadiene is subjected to an anionic telomerisation step in the presence of at least one hydrocarbyl lithium compound, at least one chain transfer-promoting catalyst and at least one chain transfer agent, thereby to form a mixture of active macromolecular carbanions and linear or substantially linear and ionically inert macromolecules, and wherein, in a further step, at least a proportion of macromolecular carbanions is reacted with a linking compound to form a multi-arm star polymer or copolymer in the presence of the linear or substantially linear inert macromolecules, said star polymer or copolymer comprising at least 5% of the total weight of the resulting polymer or copolymer.

2. A process as claimed in claim 1, wherein the hydrocarbyl lithium compound is *n*-butyl, sec-butyl lithium, or benzyl lithium.

3. A process claimed in claim 1, wherein the hydrocarbyl lithium compound is a mono- or poly-lithio polymeric hydrocarbon.

4. A process as claimed in any one of claims 1 to 3, wherein the chain transfer-promoting catalyst is toluene or xylene.

5. A process as claimed in any one of claims 1 to 4, wherein the chain transfer-promoting catalyst is an organic compound of sodium, potassium, rubidium or caesium.

6. A process as claimed in claim 5, wherein said catalyst is an alkoxide of sodium or potassium.

7. A process as claimed in any one of claims 1 to 4, wherein the chain transfer-promoting catalyst is an organic Lewis base.

8. A process as claimed in any one of claims 1 to 7, wherein the monomer is or monomers are added

gradually and at substantially the same rate at which they are consumed.

9. A process as claimed in any one of claims 1 to 8, wherein the linking compound has three or more reactive sites capable of linking with polymeric carbanions.

10. A process as claimed in any one of claims 1 to 8, wherein the linking compound is a polymerisable linking compound having at least two functional groups per molecule and capable of polymerisation to form a nucleus to which arms of the polymeric carbanion are attached.

11. A process as claimed in claim 10, wherein the polymerisable linking compound is present in an amount of at least three molecules per active carbanion.

12. A process as claimed in claim 10 to 11, wherein the linking compound is divinyl benzene.

13. A process for the preparation of a liquid polymer of butadiene or a liquid copolymer of butadiene substantially as hereinbefore described in either of the foregoing Examples.

14. A liquid polymer of butadiene or a liquid copolymer of butadiene prepared by the process claimed in any preceding claim.

15. A liquid polymer of butadiene or a liquid copolymer of butadiene as claimed in claim 14, wherein from 5 to 50% of the total weight of the polymer or copolymer is a star polymer or copolymer.

16. A liquid polymer of butadiene or a liquid copolymer of butadiene as claim 14 or 15, wherein from 10 to 25% of the total weight of the polymer or copolymer is a star polymer or copolymer.

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